

DERWENT- 2005-299172

ACC-NO:

DERWENT- 200531

WEEK:

COPYRIGHT 2006 DERWENT INFORMATION LTD

TITLE: Exhaust-gas purification system of engine, has carbon-dioxide absorber, catalyst which generates hydrogen by shift reaction of water vapor and carbon monoxide, and nitrogen-oxide catalyst, which are arranged in engine exhaust path

PATENT-ASSIGNEE: NISSAN MOTOR CO LTD[NSMO]

PRIORITY-DATA: 2003JP-0327394 (September 19, 2003)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 2005090426 A	April 7, 2005	N/A	011	F01N 003/28

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2005090426A	N/A	2003JP-0327394	September 19, 2003

INT-CL B01D053/86, B01D053/94 , B01J023/58 , B01J023/63 , B01J029/74 ,
(IPC): F01N003/08 , F01N003/10 , F01N003/20 , F01N003/28

ABSTRACTED-PUB-NO: JP2005090426A

BASIC-ABSTRACT:

NOVELTY - A **carbon-dioxide absorber**, a hydrogen generation catalyst which generates hydrogen by shift reaction of water vapor and carbon monoxide, and a

nitrogen-oxide (NOX) catalyst are arranged in engine exhaust path. A measurement unit measures temperature of the absorber and the catalysts. The (NOX) catalyst adsorbs NOX from exhaust gas, during lean state, and reduces NOX during rich state.

DETAILED DESCRIPTION - A reducing-agent supply unit intermittently increases the reducing-agent concentration in the exhaust gas. A temperature increasing unit is provided to increase the exhaust-gas temperature. The carbon-dioxide absorber is arranged at the upstream side of the hydrogen generation catalyst. The hydrogen generation catalyst is arranged such that its temperature becomes 30 deg. C or more than that of the nitrogen-oxide catalyst. The engine speed is increased after a fixed-distance travel of the motor vehicle in which the engine is arranged, to increase the exhaust-gas temperature. The carbon-dioxide absorber discharges carbon dioxide when engine temperature is increased. The engine temperature is increased by 50 deg. C or more than the temperature at which carbon dioxide is discharged by the absorber. Temperature of the absorber and the NOX catalyst is set to 700-800 deg. C and 600-750 deg. C, respectively. The absorber discharges carbon dioxide at 700 deg. C or more. The free energy of formation of the reaction of the oxide of alkali metal and/or alkaline earth metal in the nitrogen-oxide catalyst, at 300 deg. C is smaller than that of the oxide of alkali metal and/or alkaline earth metal in the hydrogen generation catalyst. The ratio of the amount of oxide, nitrate, or carbonate present in the NOX catalyst with that in the carbon-dioxide absorber, is 1:4 or more.

USE - For purifying exhaust gas of internal combustion engine of motor vehicle.

ADVANTAGE - Enables generating hydrogen also in a low-temperature area by arranging the hydrogen generation catalyst near the carbon-dioxide absorber. Enables simultaneously regenerating the nitrogen-oxide catalyst during the discharge of the carbon dioxide from the carbon-dioxide absorber. Reduces the usage amount of noble metals in the system.

DESCRIPTION OF DRAWING(S) - The figure shows a schematic view of the exhaust-gas purification system. (Drawing includes non-English language text).

CHOSEN- Dwg.1/4
DRAWING:

TITLE- EXHAUST GAS PURIFICATION SYSTEM ENGINE CARBON
TERMS: ABSORB CATALYST GENERATE HYDROGEN SHIFT REACT
WATER VAPOUR CARBON NITROGEN OXIDE CATALYST
ARRANGE ENGINE EXHAUST PATH

DERWENT-CLASS: E36 H06 J01 J04 Q51 X22

CPI-CODES: E11-D; E11-E; E11-Q02A; E31-A02C; E31-H01; E31-N05C; E31-P02B; E33; E33-A04; E34; E34-D03C; E34-D03D; E34-E; E35-L; H06-C03B; J01-E02D; J04-E09A; N01-A; N01-B; N02-E02; N02-F; N03-B02; N06-A; N06-B01; N07-B; N07-C; N07-L01C1; N07-L02C; N07-L02D;

EPI-CODES: X22-A03B; X22-A03H; X22-A05F1; X22-A07;

CHEMICAL-CODES: Chemical Indexing M3 *01* Fragmentation Code C101 C550 C810 M411 M424 M720 M740 M904 M905 N105 N209 N262 N441 N513 N514 N515 Q431 Q436 Q439 Specific Compounds 01532K 01532P Registry Numbers 1532P 1532U

Chemical Indexing M3 *02* Fragmentation Code C107 C108 C520 C730 C800 C801 C802 C803 C804 C807 M411 M424 M740 M750 M904 M905 N105 N163 Q431 Q436 Q439 Specific Compounds 01901K 01901X Registry Numbers 1901U

Chemical Indexing M3 *03* Fragmentation Code C108 C307 C520 C730 C800 C801 C802 C803 C804 C807 M411 M424 M740 M750 M904 M905 M910 N105 N163 Q431 Q436 Q439 Specific Compounds 01902K 01902X Registry Numbers 1902U

Chemical Indexing M3 *04* Fragmentation Code C107 C108 C307 C520 C730 C800 C801 C802 C803 C804 C807 M411 M424 M740 M750 M904 M905 M910 N105 N163 Q431 Q436 Q439 Specific Compounds 01881K 01881X Registry Numbers 1881U

Chemical Indexing M3 *05* Fragmentation Code C101 C108 C550 C730 C800 C801 C802 C804 C805 C807 M411 M730 M904 M905 M910 Specific Compounds 01740K 01740S Registry Numbers 1740S 1740U

Chemical Indexing M3 *06* Fragmentation Code C106 C108 C550 C730 C800 C801 C802 C803 C805 C807 M411 M730 M904 M905 M910 Specific Compounds 01423K 01423S Registry Numbers 1423S 1423U

Chemical Indexing M3 *07* Fragmentation Code C106 C108 C530 C730 C800 C801 C802 C803 C805 C807 M411 M424 M720 M740 M750 M904 M905 M910 N105 N163 N202 N209 N242 N262 N309 N343 N441 N513 N514 N515 Q431 Q436 Q439 Specific Compounds

01066K 01066P 01066X Registry Numbers 1066P 1066U

Chemical Indexing M3 *08* Fragmentation Code A758 A940 C108
C550 C730 C801 C802 C803 C804 C805 C807 M411 M424 M730
M740 M782 M904 M905 M910 N105 N163 Q421 Q431 Q436 Q439
Q508 R032 R036 Specific Compounds 01506K 01506C 01506M
01506R Registry Numbers 1506S 1506U

Chemical Indexing M3 *09* Fragmentation Code A100 A111 A200
A313 A940 B114 B701 B712 B720 B831 C108 C802 C803 C804
C805 C807 M411 M417 M423 M424 M730 M740 M782 M904 M905
N105 N163 Q421 Q431 Q436 Q439 Q508 R044 Specific Compounds
07707K 07707C 07707M 07707R A05LVK A05LVC A05LVM
A05LVR

Chemical Indexing M3 *10* Fragmentation Code A678 C810 M411
M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436
Q439 Q508 R036 Specific Compounds 03247K 03247C 03247M
03247R

Chemical Indexing M3 *11* Fragmentation Code A545 C810 M411
M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436
Q439 Q508 R036 Specific Compounds 06899K 06899C 06899M
06899R

Chemical Indexing M3 *12* Fragmentation Code A103 A540 A940
C108 C550 C730 C801 C802 C803 C804 C805 C807 M411 M424
M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439
Q508 R032 R036 Specific Compounds A40NSK A40NSC A40NSM
A40NSR

Chemical Indexing M3 *13* Fragmentation Code A111 A940 C108
C550 C730 C801 C802 C803 C804 C805 C807 M411 M424 M730
M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439 Q508
R032 R036 Specific Compounds 01517K 01517C 01517M 01517R
A28AGK A28AGC A28AGM A28AGR Registry Numbers 1517S
1517U

Chemical Indexing M3 *14* Fragmentation Code A238 A940 C108
C550 C730 C801 C802 C803 C804 C805 C807 M411 M424 M730
M740 M782 M904 M905 M910 N105 N163 Q421 Q431 Q436 Q439
Q508 R032 R036 Specific Compounds 01519K 01519C 01519M

01519R Registry Numbers 1519S 1519U

Chemical Indexing M3 *15* Fragmentation Code A212 A313 A426
A940 B114 B701 B712 B720 B831 C108 C802 C803 C804 C805
C807 M411 M424 M730 M740 M782 M904 M905 N105 N163 Q421
Q431 Q436 Q439 Q508 R044 Specific Compounds 07142K 07142C
07142M 07142R 09127K 09127C 09127M 09127R

Chemical Indexing M3 *16* Fragmentation Code A256 A940 C108
C550 C730 C800 C801 C802 C803 C804 C805 C807 M411 M424
M730 M740 M782 M904 M905 M910 N105 N163 Q421 Q431 Q436
Q439 Q508 R032 R036 Specific Compounds 01499K 01499C 01499M
01499R Registry Numbers 1499S 1499U

Chemical Indexing M3 *17* Fragmentation Code A100 A200 A940
C106 C108 C307 C510 C730 C801 C802 C803 C804 C805 C807
M411 M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431
Q436 Q439 Q508 R032 R036 Markush Compounds 200154-36401-K
200154-36401-C 200154-36401-M 200154-36401-R

Chemical Indexing M3 *18* Fragmentation Code A100 A200 A540
A940 C108 C550 C730 C801 C802 C803 C804 C805 C807 M411
M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436
Q439 Q508 R032 R036 Markush Compounds 200154-36402-K
200154-36402-C 200154-36402-M 200154-36402-R

Chemical Indexing M3 *19* Fragmentation Code A100 A200 A540
A940 C106 C108 C730 C801 C802 C803 C805 C807 M411 M424
M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439
Q508 R032 R036 Markush Compounds 200154-36403-K 200154-
36403-C 200154-36403-M 200154-36403-R

UNLINKED-DERWENT- ; 1066P ; 1066U ; 1423S ; 1423U ; 1499S ; 1499U ; 1506S ;
REGISTRY-NUMBERS: 1506U ; 1517S ; 1517U ; 1519S ; 1519U ; 1532P ; 1532U ;
1740S ; 1740U ; 1881U ; 1901U ; 1902U

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C2005-092816

Non-CPI Secondary Accession Numbers: N2005-245483

* NOTICES *

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]

It has a means to measure the temperature of the internal combustion engine which operates under a hyperoxia ambient atmosphere, CO₂ absorber, H₂ generation catalyst and the NO_x catalyst arranged in this internal combustion engine's exhaust gas passage, these CO₂ absorber and H₂ generation catalyst, and an NO_x catalyst, the reduction component increase means which can increase the reduction constituent concentration in exhaust gas intermittently, and the means which raises exhaust gas temperature,

It is the exhaust gas purification system characterized by for the above-mentioned H₂ generation catalyst generating hydrogen by the gas water gas shift reaction from a steam and a carbon monoxide, and for the above-mentioned NO_x catalyst adsorbing NO_x in the exhaust gas discharged by this internal combustion engine at the time of Lean, and carrying out reduction purification at the time of rich.

[Claim 2]

The exhaust gas purification system according to claim 1 characterized by arranging the above-mentioned H₂ generation catalyst so that it may become temperature higher 30 degrees C or more than the above-mentioned NO_x catalyst, arranging the CO₂ above-mentioned absorber in the upstream from the same part as the above-mentioned H₂ generation catalyst, or this H₂ generation catalyst, and changing.

[Claim 3]

The exhaust gas purification system according to claim 1 or 2 characterized by arranging the CO₂ above-mentioned absorber in the same part as this H₂ generation catalyst, and making the upstream into high concentration.

[Claim 4]

An exhaust gas purification system given in any one term of claims 1-3 characterized by raising an engine speed after fixed distance transit as a means which the above-mentioned internal combustion engine is car motor, and raises the above-mentioned exhaust gas temperature.

[Claim 5]

An exhaust gas purification system given in any one term of claims 1-4 to which the exhaust gas by which the temperature up was carried out with the means which raises the above-mentioned exhaust gas temperature is characterized by making CO₂ emit from the CO₂ above-mentioned absorber.

[Claim 6]

An exhaust gas purification system given in any one term of claims 1-5 characterized by being under temperature with the exhaust gas higher 50 degrees C than beyond the temperature to which CO₂ absorber emits CO₂, and its temperature by which the temperature up was carried out with the means which raises the above-mentioned exhaust gas temperature.

[Claim 7]

An exhaust gas purification system given in any one term of claims 1-6 characterized by making temperature of the CO₂ above-mentioned absorber into 700 degrees C or more less than 800 degrees C,

and making temperature of an NOx catalyst into 600 degrees C or more less than 750 degrees C.

[Claim 8]

An exhaust gas purification system given in any one term of claims 1-7 characterized by using what emits CO₂ above 700 degrees C as the CO₂ above-mentioned absorber.

[Claim 9]

An exhaust gas purification system given in any one term of claims 1-8 to which the above-mentioned H₂ generation catalyst is characterized by being the oxide, carbonate, or nitrate containing at least one sort of elements chosen from the group to which the CO₂ above-mentioned absorber changes from alkali metal and alkaline earth metal including platinum and a cerium oxide.

[Claim 10]

The exhaust gas purification system according to claim 9 characterized by for the above-mentioned alkali oxide being a multiple oxide with a zirconium, and the above-mentioned alkali carbonate being a compound carbonate with a zirconium.

[Claim 11]

The exhaust gas purification system according to claim 9 or 10 by which the CO₂ above-mentioned absorber is characterized by including platinum further.

[Claim 12]

An exhaust gas purification system given in any one term of claims 1-11 to which the CO₂ above-mentioned absorber is characterized by containing 200g or more per catalyst

[Claim 13]

The above-mentioned NOx catalyst changes including the oxide, carbonate, or nitrate containing at least one sort of elements chosen from the group which consists of platinum and/or a rhodium, a cerium oxide, and alkali metal and alkaline earth metal,

An exhaust gas purification system given in any one term of claims 1-12 characterized by free-energy-of-formation ΔG of the reaction of the oxide of the this alkali metal and/or alkaline earth metal in 300 degrees C and CO₂ being smaller than the ΔG concerned of the oxide of the alkali metal contained in H₂ generation catalyst, and/or alkaline earth metal.

[Claim 14]

The exhaust gas purification system according to claim 13 characterized by the ratio of the amount of at least one sort of oxides, carbonate or nitrate chosen from the group which consists of the alkali metal and alkaline earth metal which are contained in the above-mentioned NOx catalyst, and CO₂ absorber being 1:4 or more.

[Claim 15]

An exhaust gas purification system given in any one term of claims 1-14 by which it is characterized [which are characterized by the above-mentioned NOx catalyst containing a zeolite].

[Claim 16]

An exhaust gas purification system given in any one term of claims 1-15 to which the CO₂ above-mentioned absorber is characterized by an NOx catalyst containing barium including a lithium.

[Translation done.]

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to an exhaust gas purification system, and relates to the exhaust gas purification system which reproduces the NO_x catalyst which adsorbed and purified NO_x contained in the exhaust gas of the internal combustion engine which operates under a hyperoxia ambient atmosphere (under lean atmosphere) in the low-temperature region (200-250 degrees C), and was further made into the detail S poisoning by the pyrosphere (600-650 degrees C).

[Background of the Invention]

[0002]

NO_x is adsorbed in the Lean region and the catalyst which is made to emit NO_x at the time of SUTOIKI - rich, and is purified is known so that it may be represented by the catalyst which various catalysts which purify NO_x of the Lean region from the former are proposed, for example, supported platinum (Pt) and a lanthanum (La) to porosity support (for example, patent reference 1 reference).

[Patent reference 1] JP,5-168860,A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0003]

By the lean burn engine or the diesel power plant, NO_x has so far been purified using an NO_x adsorption catalyst. This NO_x adsorption catalyst is the following I - Ha.

b. The function to adsorb NO_x

b. The function desorbed from NO_x to which it stuck

c. The function which purifies NO_x from which it was desorbed

NO_x is purified using *****. Desorption and purification of NO_x might not take place among these functions in a low-temperature region (250 degrees C or less).

As an approach of fully ****ing and on the other hand, purifying NO_x in such a low-temperature region, use of hydrogen is effective. CO which exists in exhaust gas is specifically used, and hydrogen can be generated using a reaction called $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$.

However, in recent years, since engine combustion efficiency increased for low-fuel-consumption-izing, low emission temperature-ization progressed and CO₂ was contained in large quantities in exhaust gas, there was a trouble that a reaction could not progress easily.

[0004]

The place which this invention is made in view of the technical problem which such a conventional technique has, and is made into the purpose is to offer the exhaust gas purification system which has the NO_x decontamination capacity excellent also in the low-temperature region 250 degrees C or less.

[Means for Solving the Problem]

[0005]

this invention persons came to complete a header and this invention for the above-mentioned technical

problem being solvable by arranging CO₂ absorber with H₂ generation catalyst, as a result of repeating examination wholeheartedly that the above-mentioned technical problem should be solved.

[Effect of the Invention]

[0006]

According to this invention, H₂ generation reaction comes to advance also in a low-temperature region by making H₂ generation catalyst intermingled or arranging CO₂ absorber to near.

Moreover, this CO₂ absorber does not emit CO₂, unless it will make it an elevated temperature, once it absorbs CO₂. Therefore, although it is made an elevated temperature and CO₂ is made to emit, playback of an NO_x catalyst by which poisoning was carried out with the sulfur in exhaust gas at this time can also be performed to coincidence.

Furthermore, sulfur poisoning is canceled by easy and twist low temperature by using emitted CO₂ for re-carbonation of the NO_x adsorption component in an NO_x catalyst. Thereby, thermal resistance improves and the amount of use noble metals can be reduced.

[Best Mode of Carrying Out the Invention]

[0007]

Hereafter, the exhaust gas purification system of this invention is explained to a detail. In addition, in this specification, "%", unless it mentions specially, mass percentage is shown.

[0008]

The exhaust-gas purification system of this invention is equipped with a means measure the temperature of the internal combustion engine which operates under a hyperoxia ambient atmosphere, CO₂ absorber, H₂ generation catalyst and the NO_x catalyst arranged in this internal combustion engine's exhaust gas passage, these CO₂ absorber and H₂ generation catalyst, and an NO_x catalyst, the reduction component increase means which can increase the reduction constituent concentration in exhaust gas intermittently, and the means which raises exhaust gas temperature, and changes.

Thus, by arranging CO₂ absorber, H₂ is supplied to an NO_x catalyst from H₂ generation catalyst, and desorption / purification reaction of NO_x advances effectively also in a low-temperature region 250 degrees C or less. Moreover, an NO_x catalyst is easily reproducible by CO₂ from H₂ and CO₂ absorber from H₂ generation catalyst in the case of sulfur poisoning discharge.

[0009]

Here, the above-mentioned NO_x catalyst adsorbs NO_x in the exhaust gas discharged by the internal combustion engine by lean atmosphere, and purifies Adsorption NO_x by making it rich intermittently. In order to make it rich intermittently, it is possible to change engine operational status, to supply reduction components (H₂, CO, HC, etc.) directly, etc. For this reason, the means which raises a reduction component increase means and exhaust gas temperature is arranged, and it is intermittently made rich. In addition, the method of changing engine operational status especially is desirable, and cost can be reduced, without needing excessive equipment.

Moreover, there is also a trouble of receiving sulfur poisoning (S poisoning) in the above-mentioned NO_x catalyst. Since this S poisoning is poisoning temporarily, if it is made an elevated temperature, it can cancel, but if it puts to an elevated temperature not much, endurance will tend to fall.

If Ba which is a typical NO_x catalyst is taken for an example, S poisoning abreaction is expressed with $\text{BaSO}_4 + \text{H}_2 + \text{HC} \rightarrow \text{BaCO}_3 + \text{SO}_2$. As shown also in this formula, a sulfuric acid falls out from Ba and the function as an NO_x absorber carries out re-activity because carbonic acid enters. Here, if CO₂ is emitted H₂ generation catalyst generating hydrogen, S poisoning abreaction will progress at lower temperature.

[0010]

As the above-mentioned NO_x catalyst, what changes including platinum, a rhodium or both sides, a cerium oxide, alkali metal or alkaline earth metal and the oxide containing the thing concerning the combination of such arbitration, a carbonate, or a nitrate can be used suitably, for example.

Moreover, it is suitable for this alkali metal or alkaline earth metal that free-energy-of-formation ΔG of the reaction of those oxides and CO₂ in 250 degrees C is smaller than the ΔG concerned of the oxide of the alkali metal contained in H₂ generation catalyst or alkaline earth metal. Since CO₂ is emitted at lower temperature at this time and S poisoning discharge is also performed at low

temperature, heat-resistant ability improves.

Here, when free-energy-of-formation ΔG shows ΔG of a reaction called $A_2O + CO_2 \rightarrow A_2CO_3$ when alkali metal is set to A, and alkaline earth metal is set to B, it shows ΔG of a reaction called $BO + CO_2 \rightarrow BCO_3$. By making ΔG concerning H_2 generation catalyst small, CO_2 becomes that it is easy to be absorbed in the direction of an NO_x catalyst. In case the thing this relation of whose is the need emits CO_2 from H_2 generation catalyst at the time of S poisoning discharge, it is for an NO_x catalyst's absorbing a thing with the sufficient one as much as possible where temperature is lower, and CO_2 emitted at that temperature, and emitting S.

[0011]

Moreover, as the above-mentioned internal combustion engine, a lean burn engine, a diesel power plant, etc. are mentioned, for example. Especially when it is car motor, with the means which raises the above-mentioned exhaust gas temperature, after fixed distance transit, an engine speed can be raised and sulfur poisoning discharge can be performed. In this case, since operability is not spoiled but an emission temperature is raised effectively, it is effective. When the sulfur concentration in a gasoline is 50 ppm, about 1 time is [that what is necessary is just a time of the catalyst engine performance not exceeding a regulation value] sufficient for the timing of this sulfur poisoning discharge. [1000] As for an engine speed, it is more desirable than an engine speed in case close [of temperature up control] is not to carry out 200-800rpm extent increase. In addition, when sulfur poisoning discharge is performed frequently, there is a possibility of spoiling operability.

Furthermore, the above-mentioned internal combustion engine is usually operated under a hyperoxia ambient atmosphere (Lean region), and the exhaust gas temperature at the time of this usual operation is 200 degrees C - 250 degrees C. In this temperature region, although the adsorption reaction of NO_x advances, the reaction which *****s and purifies NO_x to which it stuck does not progress well.

Then, it is effective to arrange H_2 generation catalyst. The above-mentioned H_2 generation catalyst generates H_2 by the gas water gas shift reaction from H_2O contained in the exhaust gas at the time of rich, and CO , and can supply H_2 [effective] as reduction material which purifies Adsorption NO_x to an NO_x catalyst.

Furthermore, since, as for the latest efficient engine, an emission temperature tends to fall, the effect of CO_2 is larger still again. So, in this invention, temperature (300 degrees C or more) required for H_2 generation catalyst to fully generate hydrogen falls to about 280 degrees C by using CO_2 absorber together with the above-mentioned H_2 generation catalyst. From this, H_2 generation catalyst can arrange 280 degrees C or more and an NO_x catalyst so that it may become 200 degrees C - 250 degrees C. In addition, unless it uses CO_2 absorber, a gas water gas shift reaction does not progress easily by no less than about 10 - 14% of CO_2 contained in exhaust gas. Moreover, reduction of CO_2 amount in exhaust gas shows the data with which the amount of H_2 generation increases to drawing 3.

[0012]

As the above-mentioned H_2 generation catalyst, what contains platinum (Pt) and a cerium oxide, for example is suitable. In order to generate H_2 , adsorption of H_2O must be caused on a catalyst front face, CeO_2 is effective in it, and Pt is effective in a reaction with CO .

Moreover, as the CO_2 above-mentioned absorber, alkali metal or alkaline earth metal and the oxide containing the thing concerning the combination of such arbitration, a carbonate, or a nitrate can be used suitably, for example. Furthermore, it is desirable that the above-mentioned alkali oxide (oxide of this alkali metal or alkaline earth metal) and an alkali carbonate are compound carbonates with Zr. Zr functions as a stabilizer of alkali.

Furthermore, as for CO_2 absorber, it is desirable that Pt is included further. Since Pt desorbs S adhering to CO_2 absorber, CO_2 absorptivity ability can be demonstrated over a long period of time.

Furthermore, CO_2 absorber is good to contain 200g or more per catalyst again. In order to continue absorbing CO_2 over a long period of time, a lot of CO_2 absorbers are needed.

[0013]

Moreover, the above-mentioned H_2 generation catalyst can be arranged so that it may become temperature higher 30 degrees C or more than the above-mentioned NO_x catalyst. As for the CO_2

above-mentioned absorber, at this time, arranging in the upstream is more desirable than the same part as H₂ generation catalyst, or this H₂ generation catalyst. From this, H₂ generation fully takes place and, thereby, NO_x purification engine performance's improves. Moreover, degradation by durability can also be controlled. For example, as shown in drawing 1 and drawing 2, it can arrange. Moreover, the above-mentioned temperature control may control the rate of flow of changing the configuration of exhaust gas passage suitably, or exhaust gas, and the residence time, and may perform them. In addition, if priority is given to reaction effectiveness and H₂ generation catalyst and an NO_x catalyst are arranged in the elevated-temperature section, in order for degradation of a catalyst to advance early and to control this, a lot of noble metals must be used, and it is not desirable in respect of a resource or cost.

Furthermore, when arranging the CO₂ above-mentioned absorber in the same part as this H₂ generation catalyst, it is desirable that the upstream makes this CO₂ absorber high concentration. From this, many CO₂ are absorbed in H₂ generation catalyst preceding paragraph, H₂ generation ability of H₂ generation catalyst of the downstream increases, and the NO_x purification engine performance tends to improve.

[0014]

The means which raises the above-mentioned exhaust gas temperature may make CO₂ emit from CO₂ absorber with the exhaust gas which carried out the temperature up. That is, CO₂ absorber and H₂ generation catalyst are heated by hot exhaust gas, and S poisoning discharge temperature can be fallen by emitting CO₂ to H₂ generation and coincidence as elevated-temperature gas.

For example, what is necessary is just to heat at 620-650 degrees C by this invention, in order to use CO₂ absorber together although it is necessary to heat to 700 degrees C for S poisoning removal only with H₂ generation catalyst. As for the exhaust gas which carried out the temperature up, at this time, it is desirable that it is under temperature (less than 670-700 degrees C) higher 50 degrees C than beyond the temperature to which CO₂ absorber emits CO₂, and its temperature. It is because the catalyst engine performance will tend to deteriorate if an emission temperature is too high.

Moreover, in order to fully perform S desorption of the CO₂ emission from CO₂ absorber, or an NO_x catalyst, the CO₂ above-mentioned absorber is made into 700 degrees C or more less than 800 degrees C, and, as for an NO_x catalyst, it is desirable to consider as 600 degrees C or more less than 750 degrees C. In addition, if exhaust gas temperature is too high, it will be easy to reduce the catalyst engine performance.

Furthermore, it is desirable to use what emits CO₂ above 700 degrees C as the CO₂ above-mentioned absorber. For example, Li₂ZrO₃ etc. is mentioned.

Control of this exhaust gas temperature can be performed by interlocking the thermometry means established on each catalyst inlet port or exhaust gas passage, and the means which raises the above-mentioned exhaust gas temperature.

[0015]

Moreover, it is suitable for the ratio of the amount of the alkali metal contained in the above-mentioned NO_x catalyst or alkaline earth metal and the oxide containing the thing concerning the combination of such arbitration, a carbonate or a nitrate, and the CO₂ above-mentioned absorber that it is 1:4 or more.

Thus, H₂ and CO₂ to cancel it can be supplied. [sufficient by adjusting quantitative balance with an NO_x catalyst when the alkali in an NO_x catalyst etc. receives S poisoning]

Furthermore, as for the above-mentioned NO_x catalyst, it is desirable that a zeolite is included. From this, HC purification engine performance tends to improve in the low-temperature regions at the time of engine starting etc. (from a room temperature to 150 degrees C).

Furthermore, a lithium (Li) can be contained as the CO₂ above-mentioned absorber, and barium (Ba) can be contained as an NO_x catalyst again. These [Li and Ba] may be mixed and used.

[Example]

[0016]

Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples.

[0017]

(Example 1)

- H₂ generation catalyst with CO₂ absorber

The alumina was thrown in in the acetic-acid Ce solution, and it stirred at the room temperature for 1 hour. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 600 degrees C for 1 hour, and Powder a was obtained (Ce support concentration of this powder a is 40% as CeO₂). 2% of tetra-ammine Pt oxalate solution (pH=10.5) was sunk into Powder a. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder b was obtained (Pt support concentration of this powder b is 2.23%).

450g and alumina sol were fed to 22.5g, 900g of water was fed into the magnetic ball mill, preferential grinding of the SrO which are 427.5g and CO₂ absorber about Powder b was carried out, and the catalyst slurry was obtained.

After having made the catalyst slurry adhere to the nature monolith support of a KODEE light (1.0L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst of coat layer 400 g/L was acquired (the amount of SrO₂ in a catalyst is 200g/piece).

[0018]

- NO_x catalyst

The acetic-acid Ce water solution and the acetic-acid Ba water solution were mixed and stirred.

Subsequently, the alumina was thrown in and it stirred at the room temperature for 1 hour. Then, after drying at 120 degrees C one whole day and night, it calcinated at 600 degrees C for 1 hour, and Powder A was obtained (for Ba support concentration of Powder A, 7.3% and Ce support concentration are 20% as CeO₂ as BaO).

2% of tetra-ammine Pt oxalate solution (pH=10.5) was sunk into Powder A. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder B was obtained (Pt support concentration of Powder B is 1.04%).

The alumina was thrown in in the acetic-acid Zr water solution, and it stirred at the room temperature for 1 hour. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 900 degrees C for 1 hour. Furthermore, after sinking in 6% of nitric-acid Rh water solution, It dried at 120 degrees C one whole day and night, and calcinated at 400 degrees C for 1 hour, and Powder C was obtained (for Rh support concentration of Powder C, the support concentration of 2.4% and Zr is 3%).

After sinking 2% of tetra-ammine Pt oxalate solution (pH=10.5) into Powder A and drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder D was obtained (Pt support concentration of Powder D is 3.41%).

After sinking 2% of tetra-ammine Pt oxalate solution (pH=10.5) into cerium oxide and drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder E was obtained (Pt support concentration of Powder E is 3.2%).

92.6g and a silica sol were fed to 179.9g, 900g of water was fed into the magnetic ball mill, preferential grinding of 627.5g and the powder E was carried out for the beta zeolite, and the first catalyst slurry was obtained. Moreover, 50.5g and Oxidization Ce were fed to 47.8g and alumina sol 33.9g, 900g of water was fed into the magnetic ball mill, preferential grinding of 767.8g and the powder A was carried out for Powder B, and the second catalyst slurry was obtained. furthermore, the powder C -- 81.1g and alumina sol were fed to 58.1g, 900g of water was fed into the magnetic ball mill, preferential grinding of 272.0g and the powder D was carried out [84.8 and Oxidization Ce] for 403.9g and Powder A, and the third catalyst slurry was obtained.

After having made the first catalyst slurry adhere to the nature monolith support of a KODEE light (1.2L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst A of coat layer 172.1 g/L was acquired. After having made the second catalyst slurry adhere to this catalyst A, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst B of coat layer 167.5 g/L was acquired. After having made the third catalyst slurry adhere to this catalyst

B, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst C of coat layer 97.6 g/L was acquired.

[0019]

<The evaluation approach>

Following trial (1) - (4) was performed in order, and (3) or (4) evaluation was repeated 20 times.

(1) Durability test

The exhaust air system of an engine with a displacement of 4500 cc was equipped with the catalyst, gas oil (S= 10 ppm or less) was used, 750 degrees C and NOx catalyst inlet temperature were made into 650 degrees C, and the inlet temperature of H2 generation catalyst with CO2 absorber was operated for 50 hours.

(2) Low-temperature activity trial : room temperature -200 degree C

The exhaust air system of a diesel power plant with a displacement of 2500 cc was equipped with the catalyst, the 11 mode was run, and it asked for the rate of exhaust air purification.

(3) S poisoning, S poisoning discharge processing

After having used gas oil with an S concentration of 50 ppm, making NOx catalyst inlet temperature into 250 degrees C and performing 1hr operation, S desorption processing (gas oil S= 10 ppm or less is used, inlet temperature of 720 degrees C and an NOx catalyst is made into 650 degrees C, and the inlet temperature of H2 generation catalyst with CO2 absorber is operated for 30 minutes) was performed.

(4) Elevated-temperature activity trial : 200 degrees C - 300 degrees C

The exhaust air system of a diesel power plant with a displacement of 2500 cc was equipped with the catalyst, Lean (A/F=30) 40sec-> Rich (A/F=11) 4sec was operated, and it asked for the rate of exhaust air purification in this section.

[0020]

(Example 2)

Except having used the Pt support SrO (2% of Pt support concentration) as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0021]

(Example 3)

Except having used Li2ZrO3 as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0022]

(Example 4)

Except having used aluminum 2O3 as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0023]

(Example 5)

Except having carried out SrO in 150g/piece, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0024]

(Example 6)

Except having used Na2O as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0025]

(Example 7)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, an evaluation trial (3) and (4) were repeated and it carried out like the example 1 except the line having performed evaluation trial (3) and (S desorption processing) once twice (spacing of S poisoning discharge having been doubled).

[0026]

(Example 8)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made 650 degrees C and NOx catalyst inlet temperature into 600 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber (CO2 having been made not to be emitted from CO2 absorber).

[0027]

(Example 9)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made inlet temperature of 720 degrees C and an NOx catalyst into 580 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber.

[0028]

(Example 10)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made inlet temperature of 870 degrees C and an NOx catalyst into 650 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber.

[0029]

(Example 1 of a comparison)

Except having lost the first catalyst bed, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0030]

[Table 1]

	11モード HC転化率 (%)	(3)の処理1 回後のNOx 転化率(%)	(3)の処理20 回後のNOx 転化率(%)
実施例1	82	85	69
実施例2	80	88	75
実施例3	81	87	78
実施例4	81	83	50
実施例5	82	83	60
実施例6	81	85	52
実施例7	82	85	60
実施例8	81	80	55
実施例9	81	80	43
実施例10	82	85	62
比較例1	47	83	67

[0031]

As shown in Table 1, as for the catalyst acquired in the examples 1-10 belonging to the invention in this application, the invert ratio of HC and NOx is compatible. It turns out that especially the catalyst of examples 1-3 is excellent in the NOx invert ratio after durability. On the other hand, the first catalyst bed is not used for the catalyst acquired in the example 1 of a comparison (since there is no zeolite layer, there is no HC adsorption function.). Therefore, the cold HC engine performance gets worse. It accumulates and it turns out that HC invert ratio is low.

Moreover, if an example 1 is compared with examples 4 and 7, when the timing of the case where alkali metal is not contained in CO₂ absorber, or S poisoning discharge is behind the graph of drawing 3, it shows that the endurance of an NO_x catalyst falls.

[Brief Description of the Drawings]

[0032]

[Drawing 1] It is the schematic diagram showing an example of an exhaust gas purification system.

[Drawing 2] It is the schematic diagram showing other examples of an exhaust gas purification system.

[Drawing 3] It is the graph which shows the amount of H₂ generation to CO₂ concentration.

[Drawing 4] It is the graph which shows the relation between the count of S poisoning discharge, and an NO_x invert ratio.

[Translation done.]

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example]

[0016]

Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples.

[0017]

(Example 1)

- H₂ generation catalyst with CO₂ absorber

The alumina was thrown in in the acetic-acid Ce solution, and it stirred at the room temperature for 1 hour. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 600 degrees C for 1 hour, and Powder a was obtained (Ce support concentration of this powder a is 40% as CeO₂). 2% of tetra-ammine Pt oxalate solution (pH=10.5) was sunk into Powder a. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder b was obtained (Pt support concentration of this powder b is 2.23%).

450g and alumina sol were fed to 22.5g, 900g of water was fed into the magnetic ball mill, preferential grinding of the SrO which are 427.5g and CO₂ absorber about Powder b was carried out, and the catalyst slurry was obtained.

After having made the catalyst slurry adhere to the nature monolith support of a KODEE light (1.0L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst of coat layer 400 g/L was acquired (the amount of SrO₂ in a catalyst is 200g/piece).

[0018]

- NO_x catalyst

The acetic-acid Ce water solution and the acetic-acid Ba water solution were mixed and stirred.

Subsequently, the alumina was thrown in and it stirred at the room temperature for 1 hour. Then, after drying at 120 degrees C one whole day and night, it calcinated at 600 degrees C for 1 hour, and Powder A was obtained (for Ba support concentration of Powder A, 7.3% and Ce support concentration are 20% as CeO₂ as BaO).

2% of tetra-ammine Pt oxalate solution (pH=10.5) was sunk into Powder A. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder B was obtained (Pt support concentration of Powder B is 1.04%).

The alumina was thrown in in the acetic-acid Zr water solution, and it stirred at the room temperature for 1 hour. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 900 degrees C for 1 hour. Furthermore, after sinking in 6% of nitric-acid Rh water solution, It dried at 120 degrees C one whole day and night, and calcinated at 400 degrees C for 1 hour, and Powder C was obtained (for Rh support concentration of Powder C, the support concentration of 2.4% and Zr is 3%).

After sinking 2% of tetra-ammine Pt oxalate solution (pH=10.5) into Powder A and drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder D was

obtained (Pt support concentration of Powder D is 3.41%).

After sinking 2% of tetra-ammine Pt oxalate solution (pH=10.5) into cerium oxide and drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder E was obtained (Pt support concentration of Powder E is 3.2%).

92.6g and a silica sol were fed to 179.9g, 900g of water was fed into the magnetic ball mill, preferential grinding of 627.5g and the powder E was carried out for the beta zeolite, and the first catalyst slurry was obtained. Moreover, 50.5g and Oxidization Ce were fed to 47.8g and alumina sol 33.9g, 900g of water was fed into the magnetic ball mill, preferential grinding of 767.8g and the powder A was carried out for Powder B, and the second catalyst slurry was obtained. furthermore, the powder C -- 81.1g and alumina sol were fed to 58.1g, 900g of water was fed into the magnetic ball mill, preferential grinding of 272.0g and the powder D was carried out [84.8 and Oxidization Ce] for 403.9g and Powder A, and the third catalyst slurry was obtained.

After having made the first catalyst slurry adhere to the nature monolith support of a KODEE light (1.2L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst A of coat layer 172.1 g/L was acquired. After having made the second catalyst slurry adhere to this catalyst A, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst B of coat layer 167.5 g/L was acquired. After having made the third catalyst slurry adhere to this catalyst B, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst C of coat layer 97.6 g/L was acquired.

[0019]

<The evaluation approach>

Following trial (1) - (4) was performed in order, and (3) or (4) evaluation was repeated 20 times.

(1) Durability test

The exhaust air system of an engine with a displacement of 4500 cc was equipped with the catalyst, gas oil (S= 10 ppm or less) was used, 750 degrees C and NOx catalyst inlet temperature were made into 650 degrees C, and the inlet temperature of H2 generation catalyst with CO2 absorber was operated for 50 hours.

(2) Low-temperature activity trial : room temperature -200 degree C

The exhaust air system of a diesel power plant with a displacement of 2500 cc was equipped with the catalyst, the 11 mode was run, and it asked for the rate of exhaust air purification.

(3) S poisoning, S poisoning discharge processing

After having used gas oil with an S concentration of 50 ppm, making NOx catalyst inlet temperature into 250 degrees C and performing 1hr operation, S desorption processing (gas oil S= 10 ppm or less is used, inlet temperature of 720 degrees C and an NOx catalyst is made into 650 degrees C, and the inlet temperature of H2 generation catalyst with CO2 absorber is operated for 30 minutes) was performed.

(4) Elevated-temperature activity trial : 200 degrees C - 300 degrees C

The exhaust air system of a diesel power plant with a displacement of 2500 cc was equipped with the catalyst, Lean (A/F=30) 40sec-> Rich (A/F=11) 4sec was operated, and it asked for the rate of exhaust air purification in this section.

[0020]

(Example 2)

Except having used the Pt support SrO (2% of Pt support concentration) as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0021]

(Example 3)

Except having used Li2ZrO3 as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0022]

(Example 4)

Except having used aluminum $2O_3$ as CO_2 absorber instead of SrO , the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0023]

(Example 5)

Except having carried out SrO in 150g/piece, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0024]

(Example 6)

Except having used Na_2O as CO_2 absorber instead of SrO , the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0025]

(Example 7)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, an evaluation trial (3) and (4) were repeated and it carried out like the example 1 except the line having performed evaluation trial (3) and (S desorption processing) once twice (spacing of S poisoning discharge having been doubled).

[0026]

(Example 8)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made 650 degrees C and NO_x catalyst inlet temperature into 600 degrees C for the inlet temperature of H_2 generation catalyst with CO_2 absorber (CO_2 having been made not to be emitted from CO_2 absorber).

[0027]

(Example 9)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made inlet temperature of 720 degrees C and an NO_x catalyst into 580 degrees C for the inlet temperature of H_2 generation catalyst with CO_2 absorber.

[0028]

(Example 10)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made inlet temperature of 870 degrees C and an NO_x catalyst into 650 degrees C for the inlet temperature of H_2 generation catalyst with CO_2 absorber.

[0029]

(Example 1 of a comparison)

Except having lost the first catalyst bed, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0030]

[Table 1]

	11モード HC転化率 (%)	(3)の処理1 回後のNO _x 転化率(%)	(3)の処理20 回後のNO _x 転化率(%)
実施例1	82	85	69
実施例2	80	88	75
実施例3	81	87	78
実施例4	81	83	50
実施例5	82	83	60
実施例6	81	85	52
実施例7	82	85	60
実施例8	81	80	55
実施例9	81	80	43
実施例10	82	85	62
比較例1	47	83	67

[0031]

As shown in Table 1, as for the catalyst acquired in the examples 1-10 belonging to the invention in this application, the invert ratio of HC and NO_x is compatible. It turns out that especially the catalyst of examples 1-3 is excellent in the NO_x invert ratio after durability. On the other hand, the first catalyst bed is not used for the catalyst acquired in the example 1 of a comparison (since there is no zeolite layer, there is no HC adsorption function.). Therefore, the cold HC engine performance gets worse. It accumulates and it turns out that HC invert ratio is low.

Moreover, if an example 1 is compared with examples 4 and 7, when the timing of the case where alkali metal is not contained in CO₂ absorber, or S poisoning discharge is behind the graph of drawing 3, it shows that the endurance of an NO_x catalyst falls.

[Translation done.]

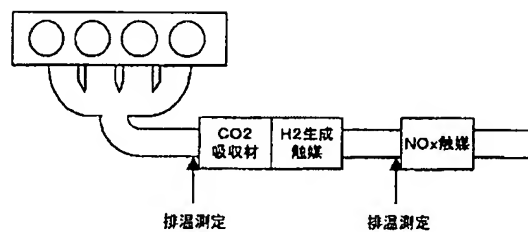
* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

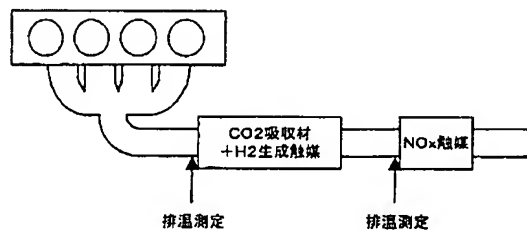
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

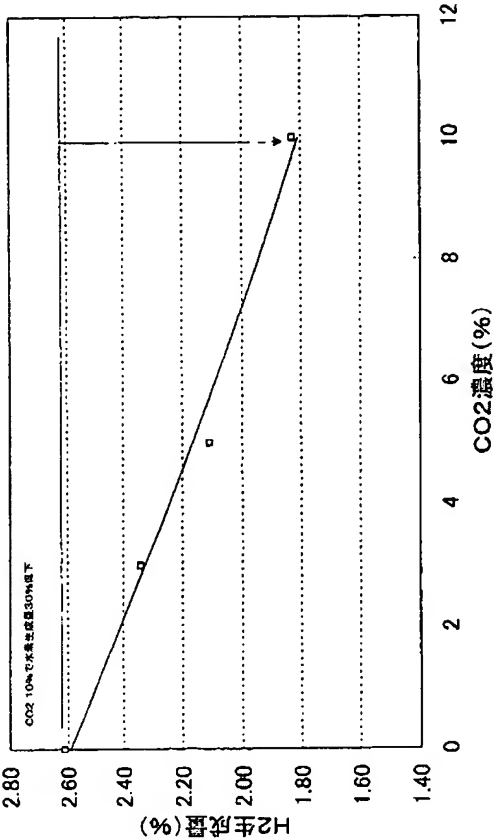
[Drawing 1]



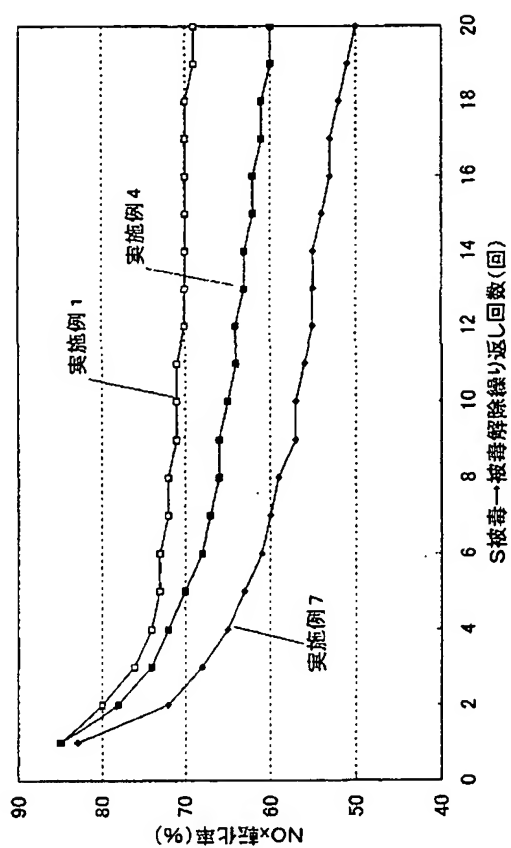
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

(19) 日本国特許庁 (JP)

(12) 公開特許公報(A)

(11) 特許出願公開番号

特開2005-90426

(P2005-90426A)

(43) 公開日 平成17年4月7日 (2005.4.7)

(51) Int. Cl. ⁷	F I	テーマコード (参考)
F O I N 3/28	F O I N 3/28 3 O I C	3 G O 9 1
B O I D 53/86	F O I N 3/28 3 O I G	4 D O 4 8
B O I D 53/94	B O I J 23/58 A	4 G O 6 9
B O I J 23/58	B O I J 29/74 A	4 G I 6 9
B O I J 23/63	F O I N 3/08 Z A B A	
審査請求 未請求 請求項の数 16 O L (全 11 頁) 最終頁に続く		

(21) 出願番号 特願2003-327394 (P2003-327394)
 (22) 出願日 平成15年9月19日 (2003.9.19)

(71) 出願人 000003997
 日産自動車株式会社
 神奈川県横浜市神奈川区宝町2番地
 (74) 代理人 100102141
 弁理士 的場 基憲
 (72) 発明者 中村 雅紀
 神奈川県横浜市神奈川区宝町2番地 日産
 自動車株式会社内
 (72) 発明者 菅 克雄
 神奈川県横浜市神奈川区宝町2番地 日産
 自動車株式会社内

最終頁に続く

(54) 【発明の名称】 排気ガス浄化システム

(57) 【要約】

【課題】 250℃以下の低温域でも優れたNO_x浄化能を有する排気ガス浄化システムを提供すること。

【解決手段】 内燃機関の排気ガス流路にCO₂吸収材、H₂生成触媒及びNO_x触媒を配設し、これらの温度を測定する手段と、還元成分増大手段と、排気ガス温度を高める手段と、を備え、H₂生成触媒が水蒸気と一酸化炭素からガスシフト反応により水素を生成し、NO_x触媒が排気ガス中のNO_xをリーン時に吸着しリッチ時に還元浄化する排気ガス浄化システムである。排気ガス温度を高める手段により昇温された排気ガスがCO₂吸収材がCO₂を放出する温度以上且つその温度よりも50℃高い温度未満である。NO_x触媒がPtやRhとCe酸化物とアルカリ金属類を含む酸化物など含み、300℃における、該アルカリ金属類の酸化物とCO₂との反応の生成自由エネルギーΔGが、H₂生成触媒に含まれるアルカリ金属類の酸化物の当該ΔGより小さいようにする。

【選択図】 なし

10

【特許請求の範囲】

【請求項 1】

酸素過剰雰囲気下で運転する内燃機関と、この内燃機関の排気ガス流路に配設する CO_2 吸収材、 H_2 生成触媒及び NO_x 触媒と、これら CO_2 吸収材、 H_2 生成触媒及び NO_x 触媒の温度を測定する手段と、排気ガス中の還元成分濃度を間欠的に増大できる還元成分増大手段と、排気ガス温度を高める手段と、を備え、

上記 H_2 生成触媒は、水蒸気と一酸化炭素からガスシフト反応により水素を生成し、上記 NO_x 触媒は、該内燃機関から排出される排気ガス中の NO_x をリーン時に吸着しリッチ時に還元浄化することを特徴とする排気ガス浄化システム。

【請求項 2】

上記 H_2 生成触媒を上記 NO_x 触媒より 30°C 以上高い温度となるように配設し、上記 CO_2 吸収材を上記 H_2 生成触媒と同じ部位又は該 H_2 生成触媒より上流側に配設して成ることを特徴とする請求項 1 に記載の排気ガス浄化システム。

【請求項 3】

上記 CO_2 吸収材を該 H_2 生成触媒と同じ部位に配設し且つ上流側ほど高濃度とすることを特徴とする請求項 1 又は 2 に記載の排気ガス浄化システム。

【請求項 4】

上記内燃機関が自動車用エンジンであって、上記排気ガス温度を高める手段として一定距離走行後にエンジン回転数を高めることを特徴とする請求項 1～3 のいずれか 1 つの項に記載の排気ガス浄化システム。

【請求項 5】

上記排気ガス温度を高める手段により昇温された排気ガスが、上記 CO_2 吸収材から CO_2 を放出させ得ることを特徴とする請求項 1～4 のいずれか 1 つの項に記載の排気ガス浄化システム。

【請求項 6】

上記排気ガス温度を高める手段により昇温された排気ガスが、 CO_2 吸収材が CO_2 を放出する温度以上且つその温度よりも 50°C 高い温度未満であることを特徴とする請求項 1～5 のいずれか 1 つの項に記載の排気ガス浄化システム。

【請求項 7】

上記 CO_2 吸収材の温度を 700°C 以上 800°C 未満とし、 NO_x 触媒の温度を 600°C 以上 750°C 未満とすることを特徴とする請求項 1～6 のいずれか 1 つの項に記載の排気ガス浄化システム。

【請求項 8】

上記 CO_2 吸収材として、 700°C 以上で CO_2 を放出するものを使用したことを特徴とする請求項 1～7 のいずれか 1 つの項に記載の排気ガス浄化システム。

【請求項 9】

上記 H_2 生成触媒が白金とセリウム酸化物を含み、上記 CO_2 吸収材がアルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも 1 種の元素を含む酸化物、炭酸塩又は硝酸塩であることを特徴とする請求項 1～8 のいずれか 1 つの項に記載の排気ガス浄化システム。

【請求項 10】

上記アルカリ酸化物がジルコニウムとの複合酸化物であり、上記アルカリ炭酸塩がジルコニウムとの複合炭酸塩であることを特徴とする請求項 9 に記載の排気ガス浄化システム。

【請求項 11】

上記 CO_2 吸収材が、更に白金を含むことを特徴とする請求項 9 又は 10 に記載の排気ガス浄化システム。

【請求項 12】

上記 CO_2 吸収材が、触媒 1 個あたり 200g 以上含まれることを特徴とする請求項 1～11 のいずれか 1 つの項に記載の排気ガス浄化システム

【請求項 13】

上記 NO_x 触媒が白金及び／又はロジウムと、セリウム酸化物と、アルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも 1 種の元素を含む酸化物、炭酸塩又は硝酸塩と、を含んで成り、

300℃における、該アルカリ金属及び／又はアルカリ土類金属の酸化物と CO_2 との反応の生成自由エネルギー ΔG が、 H_2 生成触媒に含まれるアルカリ金属及び／又はアルカリ土類金属の酸化物の当該 ΔG より小さいことを特徴とする請求項 1～12 のいずれか 1 つの項に記載の排気ガス浄化システム。

【請求項 14】

上記 NO_x 触媒に含まれるアルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも 1 種の酸化物、炭酸塩又は硝酸塩と、 CO_2 吸収材との量の比が 1：4 以上であることを特徴とする請求項 13 に記載の排気ガス浄化システム。 10

【請求項 15】

上記 NO_x 触媒がゼオライトを含むことを特徴とする特徴とする請求項 1～14 のいずれか 1 つの項に記載の排気ガス浄化システム。

【請求項 16】

上記 CO_2 吸収材がリチウムを含み、 NO_x 触媒がバリウムを含むことを特徴とする請求項 1～15 のいずれか 1 つの項に記載の排気ガス浄化システム。

【発明の詳細な説明】

【技術分野】

20

【0001】

本発明は、排気ガス浄化システムに係り、更に詳細には、酸素過剰雰囲気下（リーン雰囲気下）で運転する内燃機関の排気ガスに含まれる NO_x を低温域（200～250℃）で吸着・浄化し、高温域（600～650℃）で S 被毒された NO_x 触媒を再生する排気ガス浄化システムに関する。

【背景技術】

【0002】

従来からリーン域の NO_x を浄化する触媒は種々提案されており、例えば白金（Pt）とランタン（La）を多孔質担体に担持した触媒に代表されるように、リーン域で NO_x を吸着し、ストイキ～リッチ時に NO_x を放出させ浄化する触媒が知られている（例えば 30 特許文献 1 参照）。

【特許文献 1】特開平 5-168860 号公報

【発明の開示】

【発明が解決しようとする課題】

【0003】

これまで、リーンバーンエンジンやディーゼルエンジンでは、 NO_x 吸着触媒を使って、 NO_x の浄化を行ってきた。かかる NO_x 吸着触媒は、以下のイ～ハ

イ. NO_x を吸着する機能

ロ. 吸着した NO_x を脱離する機能

ハ. 脱離した NO_x を浄化する機能

40

の機能を使用して NO_x を浄化する。これらの機能のうち、低温域（250℃以下）では、 NO_x の脱離及び浄化が起こらないことがあった。

一方、このような低温域で NO_x を十分に脱離、浄化する方法としては、水素の利用が有効である。具体的には、排気ガス中に存在する CO を使い、 $\text{CO} + \text{H}_2 \rightarrow \text{H}_2 + \text{CO}_2$ という反応を利用して、水素を生成できる。

しかし、近年では、低燃費化のためエンジンの燃焼効率が上がり、低排温化が進み、排気ガス中に CO_2 がより大量に含まれるため、反応が進みにくいという問題点があった。

【0004】

本発明は、このような従来技術の有する課題に鑑みてなされたものであり、その目的とするところは、250℃以下の低温域でも優れた NO_x 浄化能を有する排気ガス浄化シス 50

テムを提供することにある。

【課題を解決するための手段】

【0005】

本発明者らは、上記課題を解決すべく鋭意検討を重ねた結果、 H_2 生成触媒とともに CO_2 吸収材を配設することにより、上記課題が解決できることを見出し、本発明を完成するに至った。

【発明の効果】

【0006】

本発明によれば、 CO_2 吸収材を H_2 生成触媒に混在させたり近傍に配置することにより、低温域でも H_2 生成反応が進行するようになる。

10

また、この CO_2 吸収材は一度 CO_2 を吸収すると高温にしない限り CO_2 を放出しない。よって、高温にして CO_2 を放出させるが、このときに排気ガス中の硫黄で被毒された NO_x 触媒の再生も同時に行える。

更に、放出された CO_2 を NO_x 触媒中の NO_x 吸着成分の再炭酸化に使うことで、硫黄被毒が容易且つより低温で解除される。これにより、耐熱性が向上し、使用貴金属量を低減できる。

【発明を実施するための最良の形態】

【0007】

以下、本発明の排気ガス浄化システムについて詳細に説明する。なお、本明細書において、「%」は特記しない限り質量百分率を示す。

20

【0008】

本発明の排気ガス浄化システムは、酸素過剰雰囲気下で運転する内燃機関と、この内燃機関の排気ガス流路に配設する CO_2 吸収材、 H_2 生成触媒及び NO_x 触媒と、これら CO_2 吸収材、 H_2 生成触媒及び NO_x 触媒の温度を測定する手段と、排気ガス中の還元成分濃度を間欠的に増大できる還元成分増大手段と、排気ガス温度を高める手段と、を備えて成る。

このように CO_2 吸収材を配設することで、 $250^\circ C$ 以下の低温域でも H_2 生成触媒から H_2 が NO_x 触媒に供給され、 NO_x の脱離・浄化反応が効果的に進行する。また、硫黄被毒解除の際に H_2 生成触媒からの H_2 と CO_2 吸収材からの CO_2 で NO_x 触媒を容易に再生できる。

30

【0009】

ここで、上記 NO_x 触媒は、内燃機関より排出される排気ガス中の NO_x を、リーン雰囲気で吸着し、間欠的にリッチ化することにより吸着 NO_x を浄化する。間欠的にリッチ化するには、例えば、エンジンの運転状態を変えることや、還元成分 (H_2 、 CO 及び H_2C など) を直接供給することなどが考えられる。このため、還元成分増大手段及び排気ガス温度を高める手段を配設して間欠的にリッチ化する。なお、特に、エンジンの運転状態を変える方法が望ましく、余計な装置を必要とせずコストを低減できる。

また、上記 NO_x 触媒には、硫黄被毒 (S 被毒) を受けるという問題点もある。この S 被毒は一時被毒であるため、高温にすれば解除可能であるが、あまり高温に曝すと耐久性が低下し易い。

40

代表的な NO_x 触媒である Ba を例にとれば、S 被毒解除反応は $BaSO_4 + H_2 + H_2C \rightarrow BaCO_3 + SO_2$ で表される。この式からもわかるように、Ba から硫酸が抜け、炭酸が入ることで NO_x 吸収材としての機能が再活性する。ここで、 H_2 生成触媒が水素を生成しつつ、 CO_2 を放出すれば、より低い温度で S 被毒解除反応が進むことになる。

【0010】

上記 NO_x 触媒としては、例えば、白金、ロジウムのいずれか一方又は双方と、セリウム酸化物と、アルカリ金属又はアルカリ土類金属、及びこれらの任意の組み合わせに係るものを含む酸化物、炭酸塩又は硝酸塩と、を含んで成るものを好適に使用できる。

また、該アルカリ金属やアルカリ土類金属は、 $250^\circ C$ における、それらの酸化物と CO_2 との反応の生成自由エネルギー ΔG が、 H_2 生成触媒に含まれるアルカリ金属やアル

50

カリ土類金属の酸化物の当該 ΔG より小さいことが好適である。このときは、より低い温度で CO_2 を放出し、且つ S 被毒解除も低い温度で行われるため、耐熱性能が向上する。

ここで、生成自由エネルギー ΔG とは、例えば、アルカリ金属を A とすると、 $\text{A}_2\text{O} + \text{CO}_2 \rightarrow \text{A}_2\text{CO}_3$ という反応の ΔG を示し、アルカリ土類金属を B とすると、 $\text{BO} + \text{CO}_2 \rightarrow \text{BCO}_3$ という反応の ΔG を示す。 H_2 生成触媒に係る ΔG を小さくすることで、 CO_2 が NO_x 触媒の方に吸収され易くなる。この関係が必要なのは、 S 被毒解除時、 H_2 生成触媒から CO_2 を放出する際、できるだけ温度が低い方が良く、その温度で放出された CO_2 を NO_x 触媒が吸収し S を放出するためである。

【0011】

また、上記内燃機関としては、例えば、リーンバーンエンジン及びディーゼルエンジンなどが挙げられる。特に、自動車用エンジンであるときは、上記排気ガス温度を高める手段により、一定距離走行後にエンジン回転数を高めて硫黄被毒解除を行うことができる。この場合は、運転性を損なわず効果的に排温を高められるので有効である。かかる硫黄被毒解除のタイミングは、触媒性能が規制値を超えない時点であれば良く、例えば、ガソリン中の硫黄濃度が 50 ppm である場合、 1000 km に一回程度で足りる。エンジン回転数は昇温制御の入っていない時のエンジン回転数よりも $200 \sim 800 \text{ rpm}$ 程度増大させることが望ましい。なお、硫黄被毒解除を頻繁に行うと運転性を損なう恐れがある。

更に、上記内燃機関は、酸素過剰雰囲気下（リーン域）で通常運転されるものであり、この通常運転時の排気ガス温度は $200^\circ\text{C} \sim 250^\circ\text{C}$ である。この温度域では NO_x の吸着反応は進行するものの、吸着した NO_x を脱離して浄化する反応がうまく進まない。

そこで、 H_2 生成触媒を配設するのが有効である。上記 H_2 生成触媒は、リッチ時の排気ガス中に含まれる H_2O と CO からガスシフト反応により H_2 を生成し、吸着 NO_x を浄化する還元材として有効な H_2 を NO_x 触媒へ供給し得る。

更にまた、最近の高効率エンジンは排温が低下する傾向にあるため、 CO_2 の影響はますます大きい。そこで、本発明では CO_2 吸収材を上記 H_2 生成触媒と併用することにより、 H_2 生成触媒が十分に水素を生成するのに必要な温度（ 300°C 以上）が 280°C 程度まで低下する。これより、 H_2 生成触媒は 280°C 以上、 NO_x 触媒は $200^\circ\text{C} \sim 250^\circ\text{C}$ になるように配設できる。なお、 CO_2 吸収材を使用しないと、排気ガス中に含まれる約 $10 \sim 14\%$ もの CO_2 により、ガスシフト反応がなかなか進まない。また、排気ガス中の CO_2 量が低減すると H_2 生成量が増大するデータを図3に示す。

【0012】

上記 H_2 生成触媒としては、例えば、白金（ Pt ）とセリウム酸化物を含むものが好適である。 H_2 生成するためには触媒表面上に H_2O の吸着を起こさねばならず、それには CeO_2 が有効であり、また、 CO との反応には Pt が有効である。

また、上記 CO_2 吸収材としては、例えば、アルカリ金属又はアルカリ土類金属、及びこれらの任意の組み合わせに係るものを含む酸化物、炭酸塩又は硝酸塩を好適に使用できる。更に、上記アルカリ酸化物（該アルカリ金属やアルカリ土類金属の酸化物）やアルカリ炭酸塩が Zr との複合炭酸塩であることが好ましい。 Zr はアルカリの安定剤として機能する。

更に、 CO_2 吸収材は、更に Pt を含むことが好ましい。 Pt は CO_2 吸収材に付着した S を脱離させるので、 CO_2 吸収性能を長期にわたって発揮できる。

更にまた、 CO_2 吸収材は触媒1個あたり 200 g 以上含まれることが良い。長期にわたって CO_2 を吸収し続けるためには大量の CO_2 吸収材が必要となる。

【0013】

また、上記 H_2 生成触媒は、上記 NO_x 触媒より 30°C 以上高い温度となるように配設できる。このとき、上記 CO_2 吸収材は H_2 生成触媒と同じ部位又は該 H_2 生成触媒より上流側に配設することが好ましい。これより、 H_2 生成が十分に起こり、それにより NO_x 浄化性能も向上する。また、耐久による劣化も抑制できる。例えば、図1及び図2に示すように配設できる。また、上記温度調節は、排気ガス流路の形状を適宜変更することや排気ガスの流速、滞留時間を制御して行っても良い。なお、反応効率を優先し、高温部に

H₂ 生成触媒やNO_x 触媒を配置すると触媒の劣化が早く進行し、これを抑制するためには大量の貴金属を使わなければならない、資源面でもコストの面でも望ましくない。

更に、上記CO₂ 吸収材を該H₂ 生成触媒と同じ部位に配設するときは、上流側ほど該CO₂ 吸収材を高濃度とすることが好ましい。これより、H₂ 生成触媒前段で多くのCO₂ を吸収し、下流側のH₂ 生成触媒のH₂ 生成能が高まり、NO_x 浄化性能が向上し易い。

【0014】

上記排気ガス温度を高める手段は、昇温した排気ガスによりCO₂ 吸収材からCO₂ を放出させ得る。即ち、高温の排気ガスによりCO₂ 吸収材及びH₂ 生成触媒が加熱され、H₂ 生成と同時にCO₂ が高温ガスとして放出されることにより、S 被毒解除温度を低下

10

できる。
例えば、H₂ 生成触媒のみではS 被毒除去には700℃まで加熱する必要があるが、本発明ではCO₂ 吸収材を併用するため620～650℃に加熱すれば良い。このとき、昇温した排気ガスは、CO₂ 吸収材がCO₂ を放出する温度以上且つその温度よりも50℃高い温度未満（670～700℃未満）であることが好ましい。排温が高すぎると触媒性能が劣化し易いからである。

また、CO₂ 吸収材からのCO₂ 放出やNO_x 触媒のS 脱離を十分に行うためには、上記CO₂ 吸収材は700℃以上800℃未満とし、NO_x 触媒は600℃以上750℃未満とすることが好ましい。なお、排気ガス温度が高過ぎると触媒性能を低下させ易い。

更に、上記CO₂ 吸収材としては、700℃以上でCO₂ を放出するものを使用することが好ましい。例えばLi₂ZrO₃ などが挙げられる。

20

かかる排気ガス温度の制御は、各触媒入口や排気ガス流路上に設けた温度測定手段と、上記排気ガス温度を高める手段を連動させて行うことができる。

【0015】

また、上記NO_x 触媒に含まれるアルカリ金属又はアルカリ土類金属、及びこれらの任意の組み合わせに係るものを含む酸化物、炭酸塩又は硝酸塩と、上記CO₂ 吸収材との量の比は、1：4以上であることが好適である。このように、NO_x 触媒との量的バランスを調整することで、NO_x 触媒中のアルカリなどがS 被毒を受けたときに、それを解除するのに十分なH₂ 及びCO₂ を供給できる。

更に、上記NO_x 触媒は、ゼオライトを含むことが好ましい。これより、エンジン始動時等の低温域（室温から150℃）において、HC 浄化性能が向上し易い。

30

更にまた、上記CO₂ 吸収材としてリチウム（Li）を含有し且つNO_x 触媒としてバリウム（Ba）を含有することができる。これらLiとBaを混合して使用しても良い。

【実施例】

【0016】

以下、本発明を実施例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【0017】

（実施例1）

・CO₂ 吸収材付きH₂ 生成触媒

40

アルミナを酢酸Ce 溶液の中に投入し、1時間室温で攪拌した。次いで、120℃で一昼夜乾燥した後、600℃で1時間焼成し粉末aを得た（この粉末aのCe 担持濃度はCeO₂ として40%）。

粉末aに2%のテトラアンミンPt 水酸塩溶液（pH=10.5）を含浸した。次いで、120℃で一昼夜乾燥した後、400℃で1時間焼成し粉末bを得た（この粉末bのPt 担持濃度は2.23%）。

粉末bを427.5g、CO₂ 吸収材であるSrOを450g、アルミナゾルを22.5g、水900gを磁性ボールミルに投入し、混合粉碎して、触媒スラリを得た。

触媒スラリをコーデライト質モノリス担体（1.0L、400セル）に付着させ、空気流にてセル内の余剰のスラリを取り除いて130℃で乾燥した後、400℃で1時間焼

50

成し、コート層 400 g/L の触媒を得た（触媒中の SrO_2 の量は 200 g/個である）。

【0018】

・ NO_x 触媒

酢酸 Ce 水溶液と酢酸 Ba 水溶液を混合し、攪拌した。次いで、アルミナを投入し、1 時間室温で攪拌した。その後、120℃で一昼夜乾燥した後、600℃で1時間焼成し、粉末 A を得た（粉末 A の Ba 担持濃度は BaO として 7.3%、 Ce 担持濃度は CeO_2 として 20%）。

粉末 A に 2% のテトラアンミン Pt 水酸塩溶液（ $\text{pH} = 10.5$ ）を含浸した。次いで、120℃で一昼夜乾燥した後、400℃で1時間焼成し粉末 B を得た（粉末 B の Pt 担持濃度は 1.04%）。 10

酢酸 Zr 水溶液中にアルミナを投入し、1 時間室温で攪拌した。次いで、120℃で一昼夜乾燥した後、900℃で1時間焼成した。更に、6% の硝酸 Rh 水溶液を含浸した後、120℃で一昼夜乾燥し、400℃で1時間焼成し粉末 C を得た（粉末 C の Rh 担持濃度は 2.4%、 Zr の担持濃度は 3%）。

粉末 A に 2% のテトラアンミン Pt 水酸塩溶液（ $\text{pH} = 10.5$ ）を含浸し、120℃で一昼夜乾燥した後、400℃で1時間焼成し粉末 D を得た（粉末 D の Pt 担持濃度は 3.41%）。 20

酸化セリウムに 2% のテトラアンミン Pt 水酸塩溶液（ $\text{pH} = 10.5$ ）を含浸し、120℃で一昼夜乾燥した後、400℃で1時間焼成し粉末 E を得た（粉末 E の Pt 担持濃度は 3.2%）。 30

ベータゼオライトを 627.5 g、粉末 E を 92.6 g、シリカゾルを 179.9 g、水 900 g を磁性ボールミルに投入し、混合粉砕して、第一触媒スラリを得た。また、粉末 B を 767.8 g、粉末 A を 50.5 g、酸化 Ce を 47.8 g、アルミナゾル 33.9 g、水 900 g を磁性ボールミルに投入し、混合粉砕して、第二触媒スラリを得た。更に、粉末 C を 272.0 g、粉末 D を 403.9 g、粉末 A を 84.8 g、酸化 Ce を 81.1 g、アルミナゾルを 58.1 g、水 900 g を磁性ボールミルに投入し、混合粉砕して、第三触媒スラリを得た。

第一触媒スラリをコーデライト質モノリス担体（1.2 L、400セル）に付着させ、空気流にてセル内の余剰のスラリを取り除いて130℃で乾燥した後、400℃で1時間焼成し、コート層 172.1 g/L の触媒 A を得た。この触媒 A に第二触媒スラリを付着させ、空気流にてセル内の余剰のスラリを取り除いて130℃で乾燥した後、400℃で1時間焼成し、コート層 167.5 g/L の触媒 B を得た。この触媒 B に第三触媒スラリを付着させ、空気流にてセル内の余剰のスラリを取り除いて130℃で乾燥した後、400℃で1時間焼成し、コート層 97.6 g/L の触媒 C を得た。 40

【0019】

<評価方法>

以下の試験（1）～（4）を順に行い、（3）、（4）の評価は20回繰り返した。

（1）耐久試験 40

排気量 4500 cc のエンジンの排気系に触媒を装着し、軽油（ $\text{S} = 10 \text{ ppm}$ 以下）を使用し、 CO_2 吸収材付き H_2 生成触媒の入口温度を 750℃、 NO_x 触媒入口温度を 650℃とし、50 時間運転した。

（2）低温活性試験：室温～200℃

排気量 2500 cc のディーゼルエンジンの排気系に触媒を装着して、11 モードを走り、排気浄化率を求めた。

（3） S 被毒、 S 被毒解除処理

S 濃度 50 ppm の軽油を使用し、 NO_x 触媒入口温度を 250℃とし、1 hr 運転を行った後、 S 脱離処理（ $\text{S} = 10 \text{ ppm}$ 以下の軽油を使用し、 CO_2 吸収材付き H_2 生成触媒の入口温度を 720℃、 NO_x 触媒の入口温度を 650℃とし、30 分運転）を行っ 50

た。

(4) 高温活性試験：200℃～300℃

排気量2500ccのディーゼルエンジンの排気系に触媒を装着して、リーン(A/F=30)40sec→リッチ(A/F=11)40secの運転を行い、この区間における排気浄化率を求めた。

【0020】

(実施例2)

SrOの代わりにPt担持SrO(Pt担持濃度2%)をCO₂吸収材として使用した以外は、実施例1と同様の操作を繰り返して触媒を得た。また、同様の評価方法を行った。

10

【0021】

(実施例3)

SrOの代わりにLi₂ZrO₃をCO₂吸収材として使用した以外は、実施例1と同様の操作を繰り返して触媒を得た。また、同様の評価方法を行った。

【0022】

(実施例4)

SrOの代わりにAl₂O₃をCO₂吸収材として使用した以外は、実施例1と同様の操作を繰り返して触媒を得た。また、同様の評価方法を行った。

【0023】

(実施例5)

SrOを150g/個とした以外は、実施例1と同様の操作を繰り返して触媒を得た。また、同様の評価方法を行った。

20

【0024】

(実施例6)

SrOの代わりにNa₂OをCO₂吸収材として使用した以外は、実施例1と同様の操作を繰り返して触媒を得た。また、同様の評価方法を行った。

【0025】

(実施例7)

実施例1と同様の操作を繰り返して触媒を得た。また、評価方法については、評価試験(3)、(4)を繰り返し2回行って、評価試験(3)(S脱離処理)を1回行った(S被毒解除の間隔を2倍にした)以外は、実施例1と同様に行った。

30

【0026】

(実施例8)

実施例1と同様の操作を繰り返して触媒を得た。また、評価方法については、評価試験(3)のS脱離処理時の温度をCO₂吸収材付きH₂生成触媒の入口温度を650℃、NOx触媒入口温度を600℃とした(CO₂吸収材からCO₂が放出されないようにした)以外は、実施例1と同様に行った。

【0027】

(実施例9)

実施例1と同様の操作を繰り返して触媒を得た。また、評価方法については、評価試験(3)のS脱離処理時の温度をCO₂吸収材付きH₂生成触媒の入口温度を720℃、NOx触媒の入口温度を580℃とした以外、実施例1と同様に行った。

40

【0028】

(実施例10)

実施例1と同様の操作を繰り返して触媒を得た。また、評価方法については、評価試験(3)のS脱離処理時の温度をCO₂吸収材付きH₂生成触媒の入口温度を870℃、NOx触媒の入口温度を650℃とした以外、実施例1と同様に行った。

【0029】

(比較例1)

第一触媒層を無くした以外、実施例1と同様の操作を繰り返して触媒を得た。また、同

50

様の評価方法を行った。

【0030】

【表1】

	11モード HC転化率 (%)	(3)の処理1 回後のNO _x 転化率(%)	(3)の処理20 回後のNO _x 転化率(%)
実施例1	82	85	69
実施例2	80	88	75
実施例3	81	87	78
実施例4	81	83	50
実施例5	82	83	60
実施例6	81	85	52
実施例7	82	85	60
実施例8	81	80	55
実施例9	81	80	43
実施例10	82	85	62
比較例1	47	83	67

10

20

【0031】

表1に示すように、本願発明に属する実施例1～10で得られた触媒は、HC及びNO_xの転化率が両立されている。特に、実施例1～3の触媒は、耐久後のNO_x転化率が優れることがわかる。一方、比較例1で得られた触媒は、第一触媒層を用いていない（ゼオライト層がないためHC吸着機能がない。よってコールドHC性能が悪化する。）ため、HC転化率が低いことがわかる。

また、図3のグラフより、実施例1と実施例4、7を比較すると、CO₂吸収材にアルカリ金属が含まれない場合やS被毒解除のタイミングが遅れている場合は、NO_x触媒の耐久性が低下することがわかる。

【図面の簡単な説明】

30

【0032】

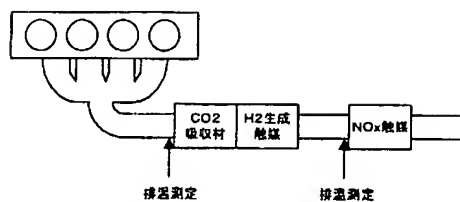
【図1】排気ガス浄化システムの一例を示す概略図である。

【図2】排気ガス浄化システムの他の例を示す概略図である。

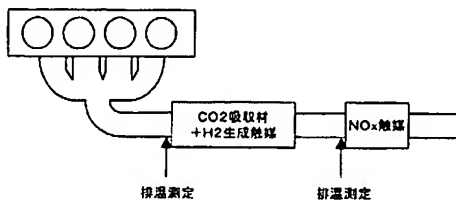
【図3】CO₂濃度に対するH₂生成量を示すグラフである。

【図4】S被毒解除の回数とNO_x転化率との関係を示すグラフである。

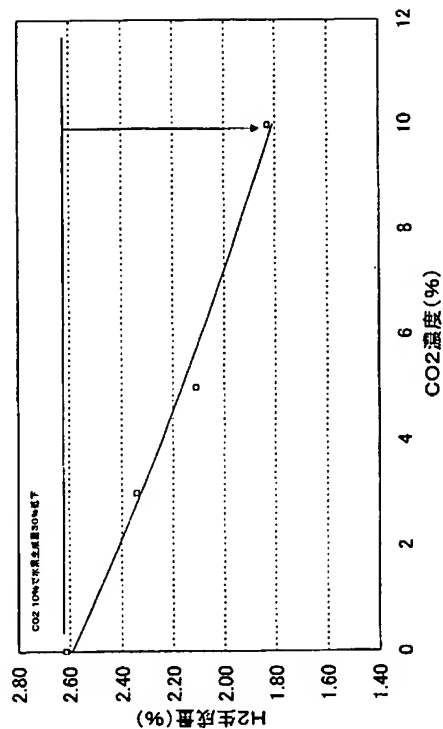
【図 1】



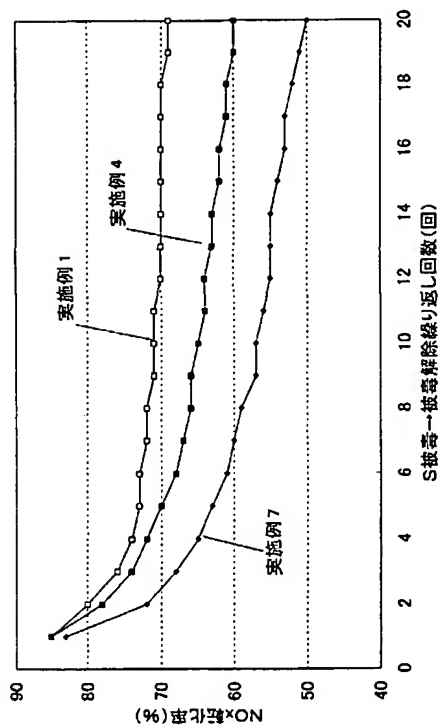
【図 2】



【図 3】



【図 4】



フロントページの続き

(51)Int. Cl.⁷

F I

テーマコード (参考)

B O 1 J	29/74	F O 1 N	3/10	A
F O 1 N	3/08	F O 1 N	3/20	E
F O 1 N	3/10	B O 1 D	53/36	1 0 4 A
F O 1 N	3/20	B O 1 D	53/36	K
		B O 1 J	23/56	3 0 1 A
		B O 1 D	53/36	1 0 2 H

F ターム(参考) 3G091 AA17 AA18 AB05 AB08 BA01 BA11 BA14 EA17 EA19 FB02
 FB05 FC07 FC08 GA06 GB01W GB02W GB03W GB05W GB06W GB09W
 GB10W GB13W HA08 HA20

4D048 AA06 AA13 AA18 AB02 AB05 AB06 AB07 BA01Y BA02Y BA11X
 BA14X BA15X BA19X BA30X BA33X BA41X BA45Y BA46X BB02 BC01
 BD01 BD02 CC32 CC36 CC41 CC46 CC52 CD01 CD10 DA01
 DA02 DA03 DA06 DA08 DA13 DA20 EA04

4G069 AA03 AA08 BA01B BA02B BA05B BA07B BB04A BB04B BB06B BB12A
 BB16A BC01A BC02B BC04B BC08A BC12B BC13A BC13B BC43A BC43B
 BC51B BC71A BC71B BC75A BC75B BD02A BD04A BD06A CA03 CA09
 CC26 DA06 EA19 EC28 FA01 FA02 FA03 FB14 FB15 FB19
 FB30 ZA19B

4G169 AA03 AA08 BA01B BA02B BA05B BA07B BB04A BB04B BB06B BB12A
 BB16A BC01A BC02B BC04B BC08A BC12B BC13A BC13B BC43A BC43B